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(54) LITHIUM SECONDARY BATTERY NEGATIVE ELECTRODE MATERIAL AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium secondary battery negative electrode material and its manufacturing method in which charge and discharge capacity is large, and battery performance having excellent cycle characteristics is equipped.

SOLUTION: Lithium secondary battery negative electrode material is made of carbon material in which its carbon fiber surface is coated by the carbide of thermosetting resin, a lattice spacing (d002) value by X-ray diffraction is d002<0.343nm at a carbon fiber portion, d002 <0.340nm at a resin carbonized portion, and weight ratios of carbon fiber and resin carbide are 1:0.5 to 2. Solution prepared by dissolving the thermosetting resin in organic solvent is impregnated into a carbon fiber sheet, is cured so as to coat the carbon fiber surface by the thermosetting resin, and the same is carbonized in temperatures from 2,000 to 3,000°C in a non-oxidizing atmosphere so as to manufacture the negative electrode material.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]The charge-and-discharge capacity of this invention which made lithium support the carbon material of the compound presentation structure where the carbon fiber surface was covered with the carbide of thermosetting resin is large, and it relates to the negative electrode material for lithium secondary batteries provided with the outstanding cycle characteristic, and its manufacturing method.

[0002]

[Description of the Prior Art]In recent years, the lithium secondary battery which has high energy density attracts attention as the power supply of sized electronic equipment, or a cell for stationary energy storage, and development is furthered. Although the lithium metal was used at the beginning, while repeating charge and discharge in the negative electrode of a lithium secondary battery, lithium [activity / arborescence / which is called a dendrite to a negative electrode] deposits in it, a short circuit with the anode by exfoliation and growth of this dendrite that deposited takes place to it, and there is a problem to which a cycle characteristic falls in it.

[0003]In order to prevent the deposit of a dendrite, there is also the method of using a lithium alloy as a negative electrode material, but there is a fault which is not enough, Then, it becomes clear that generation of a dendrite will be prevented if a carbon material is used, Research which makes a carbon material of a certain kind support lithium which is negative electrode active material, and is used as a negative electrode material is done briskly, the description of a support carbon material -- many proposals (for example, JP,62-90863,A.) A 62-193463 gazette, a 63-236259 gazette, a 64-2258 gazette, JP,1-274360,A, and the 2-44644 An item gazette and the 2-66856 An item gazette, a 2-230660 gazette, and the 3-93162 The item gazette etc. are made.

[0004]Since between the graphite layers of a hex-steel plane structure is developed, the black lead of high crystallinity represented by natural graphite as a carbon material shows the cell capacity more than 300 mAh/g theoretically, and also it is excellent also in the surface smoothness of potential. Since it is fibrous when carbon fiber is used as a negative electrode, and contact between textiles becomes good and contact resistance falls, it is comparatively alike and is observed as a negative pole material of big cell capacity.

[0005]For example, it is the negative electrode for lithium secondary batteries (JP,4-359862,A) and sheet-shaped carbon fiber content carbon material which were constituted by the section where an electrode surface

is vertical to the fiber axis of a carbon fiber aggregate which arranged the fiber axis in parallel as a negative electrode material of the lithium secondary battery using carbon fiber, The negative electrode for lithium secondary batteries (JP,7-22022,A) etc. in which carbon fiber is carrying out orientation in parallel with the surface of this sheet are proposed.

[0006]If the degree of graphitization of carbon fiber is raised, while the high cell capacity about 300 mAh/g will be obtained, the degree which the edge face of black lead structure exposes to an electrode surface becomes large, and there is a fault to which early charge and discharge efficiency falls, and also there is a difficulty which cannot respond to the request of high-capacity-izing in recent years in a carbon fiber independent.

[0007]Then, the carbon material of polyphase structure using carbon fiber etc. as a negative electrode material is developed, For example, the negative electrode for the lithium secondary batteries which coated with the thin film of amorphous carbon the surface of the carbon material used as a component of a negative electrode (JP,5-275076,A) and the carbonaceous material which forms a core, Have the polyphase structure which consists of at least 2 phases of the carbonaceous material of the surface formed in the surface of this core, and spacing d_{002} of a field (002) 3.35-A or more the peak below 3.43 A, The carbonaceous material in which d_{002} has at least two peaks of a peak of 3.43 A or more (JP,5-290889,A), The electrode material (JP,6-267531,A) of polyphase structure etc. in which d_{002} covered the particles of carbonaceous material of 3.37 A or less with carbonaceous material of 3.38 A or more in d_{002} are proposed.

[0008]

[Problem(s) to be Solved by the Invention]Each carbon material which has such polyphase structures uses high carbon of a degree of graphitization as an inner core, Low carbon of the degree of graphitization is formed in the surface, carbon with two or more fibrous degrees of graphitization high to above-mentioned JP,5-290889,A is used as an inner core, and the model of the polyphase structure which carbon whose degree of graphitization is lower than it included is shown.

[0009]The high carbon material of such a degree of graphitization is used as an intension thing, and if the carbon material of the 2-phase structure which covered the carbon material of the quality of amorphous whose degree of graphitization is lower than this is used as a negative electrode material for lithium secondary batteries, irnprovement in a cycle characteristic can be aimed at. However, in order that between the graphite layers inside a high degree of graphitization may expand by the dope of the adsorption and desorption of the lithium ion at the time of charge and discharge, especially the lithium ion at the time of charge and between graphite layers may contract conversely at the time of discharge, damage and destruction arise by repetition of charge and discharge, and there is a limit in raising cell capacity.

[0010]If charge-and-discharge capacity is large, and carbon fiber is covered and calcinated with the thermosetting resin of difficulty graphitization nature, this invention person maintaining the moldability which was excellent in carbon fiber as a result of inquiring wholeheartedly about the negative electrode material excellent in the cycle characteristic for lithium secondary batteries, The resinous coal-ized part became a carbon layer with a comparatively high degree of graphitization, and it found out that charge-and-discharge capacity and a cycle characteristic improved.

[0011]This invention is developed based on the above-mentioned knowledge, the purpose has large charge-

and-discharge capacity, and it is in providing the negative electrode material for lithium secondary batteries provided with the outstanding cycle characteristic, and its manufacturing method.

[0012]

[Means for Solving the Problem]A negative electrode material for lithium secondary batteries of this invention for attaining the above-mentioned purpose, A carbon fiber surface is covered with carbide of thermosetting resin, and a value of lattice spacing (d_{002}) by an X diffraction by a carbon fiber part d_{002}<0.343nm, It is d_{002}<0.340nm in a resinous coal-ized part, and is characterized [constitutional] by a weight ratio of carbon fiber and a resinous coal ghost consisting of a carbon material of 1:0.5-2.

[0013]The manufacturing method impregnates with and hardens a solution which dissolved thermosetting resin in an organic solvent to a carbon fiber sheet, Laminate thermosetting resin on a carbon fiber surface, and a carbon fiber surface is covered with carbide of thermosetting resin by subsequently carbonizing at temperature of 2000-3000 ** among a non-oxidizing atmosphere, A value of lattice spacing (d_{002}) by an X diffraction is characterized [constitutional] by a weight ratio of d_{002}<0.340nm and carbon fiber, and a resinous coal ghost obtaining a carbon material of 1:0.5-2 in d_{002}<0.343nm and a resinous coal-ized part by a carbon fiber part.

[0014]

[Embodiment of the Invention]The negative electrode material for lithium secondary batteries of this invention comprises 2-phase structure with which the surface of carbon fiber was covered by the carbide of thermosetting resin, The thing for which the value of lattice spacing (d_{002}) is provided with d_{002}<0.340nm graphite-crystals description in d_{002}<0.343nm and a resinous coal-ized part by the carbon fiber part and to require has the feature. Namely, compared with the degree of graphitization of a carbon fiber part, the degree of graphitization of the carbide of the thermosetting resin which covers the surface is relatively characterized by a high point, The new occlusion site of a lithium ion occurs by both interaction, and improvement in charge-and-discharge capacity is brought about, and also the surface smoothness of improvement in early current efficiency or the potential of a charge-and-discharge curve becomes good. The effect of such an interaction is small and it becomes impossible for the value of a degree of graphitization (d_{002}) to increase cell capacity by a carbon fiber part, as it is 0.340 nm or more in 0.343 nm or more and a resinous coal-ized part. The lattice spacing (d_{002}) showing a degree of graphitization is ** ** by carrying out peak resolution of the 002 diffraction lines corresponding between the carbon layers by an X diffraction.

[0015]The weight ratio of carbon fiber and a resinous coal ghost needs to be in the range of 1:0.5-2. since less than 0.5 are not enough as covering of a resinous coal ghost, the effect of an interaction has a small weight ratio of a resinous coal ghost, if 2 is exceeded on the other hand, the rate of a carbon fiber part will decrease, charge-and-discharge capacity will fall, and early current efficiency will also become small.

[0016]The negative electrode material for lithium secondary batteries of this invention is manufactured by heat-treating and graphitizing [carbonize and] at the temperature of 2000-3000 ** in a non-oxidizing atmosphere, after impregnating and carrying out heat cure of the solution which dissolved thermosetting resin in the organic solvent to a carbon fiber sheet and laminating thermosetting resin on a carbon fiber surface. It is because the

improvement in a degree of graphitization is seldom no longer accepted even if it heat-treats at the temperature which becomes insufficient [a degree of graphitization] and exceeds 3000 **, when heat treatment temperature is less than 2000 **.

[0017]Although the carbon fiber in particular used by this invention is not limited and can use both polyacrylonitrile system carbon fiber rayon system carbon fiber and a pitch based carbon fiber, Since the diffusion rate of a lithium ion becomes it large that the arraying structure of the crystal in the cross section of carbon fiber is radial (radiate) structure, it is desirable.

[0018]As for thermosetting resin, thermosetting resin, such as phenol system resin of not less than 50% of difficulty graphitization nature, furan system resin, polyimide resin, and poly carbodiimide resin, is used for an actual carbon ratio, and phenol resin or furan resin is used preferably. It is because an actual carbon ratio cannot fully cover a carbon fiber surface with a resinous coal ghost at less than 50%. These thermosetting resin Methanol, ethanol, benzene, acetone, The solution which dissolved in concentration proper to organic solvents, such as toluene, is applied to a carbon fiber sheet, or it is impregnated by the method of a carbon fiber sheet being immersed into a solution, and it heats, and it hardens and dries and thermosetting resin is laminated on a carbon fiber surface. The amount of being impregnated is set up so that the resinous coal ghost after carbonization and graphitization may serve as the range of 0.5-2 to the carbon fiber 1 by a weight ratio.

[0019]Subsequently, the surface of carbon fiber is covered with the carbide of thermosetting resin by heating in temperature of 2000-3000 **, calcinating, and carbonizing and graphitizing the covered thermosetting resin in non-oxidizing atmospheres, such as argon and nitrogen gas. Although a volumetric shrinkage happens in process of carbonization and graphitization, thermosetting resin, Since the volumetric shrinkage of carbon fiber is small compared with thermosetting resin, it carbonizes under moderate turgescence, The degree of graphitization of a carbon fiber part and a resinous coal ghost, without graphitization advancing and a resinous coal ghost exfoliating The graphite-crystals description of this invention, That is, the value of lattice spacing (d_{002}) can consider it as d_{002}<0.340nm graphite-crystals description in d_{002}<0.343nm and a resinous coal-ized part by a carbon fiber part. It is because less than 2000 ** of heat treatment temperature is [carbonization and graphitization] insufficient and heat treatment at the temperature over 3000 ** is unnecessary. Thus, the carbon material which covered the acquired carbon fiber surface with the resinous coal ghost is ground in a proper size, and the negative electrode material for lithium secondary batteries of this invention is manufactured.

[0020]Since the negative electrode material for lithium secondary batteries of this invention has little exposure of the edge face in the surface by making into a suitable degree of graphitization the resinous coal ghost covered to the carbon fiber surface, a reaction with an electrolysis solution is inhibited and decline in the current efficiency in the first stage is prevented. The occlusion site of a lithium ion increases by the interaction of carbon fiber and the resinous coal ghost covered by the surface, the cell capacity at the time of charge and discharge increases, and improvement in the surface smoothness of the potential at the time of charge and discharge and the difference of charge and discharge become possible [becoming large and aiming at control of irreversible capacity]. Expansion of the carbon fiber by the adsorption and desorption of the lithium ion at the time of charge and discharge and destruction by contraction are prevented, and a cycle characteristic can

be raised.

[0021]Thus, the negative electrode material for lithium secondary batteries of this invention, Since a carbon fiber surface makes lithium support the carbon material of the compound presentation structure where it was covered with the carbide of thermosetting resin and the degree of graphitization was specified, It is possible to aim at increase of charge-and-discharge capacity, improvement in a cycle characteristic, etc., and since the fibrous form is also held, contact resistance is also maintainable to lower order.

[0022]

[Example]Hereafter, it explains concretely, contrasting the example of this invention with a comparative example.

[0023]The pitch based carbon fiber which carried out the chop to 3 mm in length as one to Examples 1-9 and comparative example 3 carbon fiber [The product made from Japanese Graphite fiber, XN-40] And polyacrylonitrile system carbon fiber It distributes these chopped carbon fiber in ethanol and dried [filtered and] using [the Toray Industries, Inc. make and T300], and the carbon fiber sheet was created. To this carbon fiber sheet, it is phenol resin of 50% of an actual carbon ratio. It was made to be impregnated, and it heated, and the solution (resin concentration 5 to 40 % of the weight) which dissolved [the product made from Sumitomo DEYUREZU and PR940] in acetone was hardened and dried so that the weight ratio of a pitch might be set to 0.6-2.5 to the carbon fiber 1. Thus, the carbon fiber chop which laminated phenol resin was changed, heat-treated and graphitized [carbonized and] for temperature in 1800-3000 ** in a nitrogen atmosphere. Thus, the graphitization characteristic of the carbon material obtained about the carbon fiber chop which covered the carbide of the manufactured phenol resin by measuring the lattice spacing (d_{002}) of a carbon fiber part and a resinous coal-ized part according to an X diffraction was shown in Table 1 as contrasted with manufacturing conditions.

[0024]

[Table 1]

例No.		炭素繊維種	被覆樹脂種 *1	熱処理温度 (℃)	炭素材		
					重量比 *2	格子面間隔(nm)	
						炭素繊維部	樹脂炭化部
比	1	XN-40	Ph-1	1800	1.0/1	0.342	0.341
実	1	XN-40	Ph-1	2000	1.0/1	0.340	0.339
実	2	XN-40	Ph-1	2500	1.0/1	0.336	0.338
実	3	XN-40	Ph-1	3000	1.0/1	0.335	0.337
比	2	XN-40	Ph-1	2500	0.3/1	0.336	0.337
実	4	XN-40	Ph-1	2500	0.5/1	0.336	0.338
実	5	XN-40	Ph-1	2500	1.0/1	0.336	0.338
実	6	XN-40	Ph-1	2500	2.0/1	0.336	0.339
比	3	XN-40	Ph-1	2500	2.3/1	0.336	0.339
実	7	T-300	Ph-1	2000	1.0/1	0.342	0.340
実	8	T-300	Ph-1	2500	1.0/1	0.341	0.338
実	9	T-300	Ph-1	3000	1.0/1	0.340	0.337

Front notes *1 Ph-1; phenol resin of 50% of an actual carbon ratio Weight ratio of *2 resinous-coal ghost and carbon fiber[0025]Grind the carbon fiber chop which covered the carbide of this phenol resin so that mean fiber length may be set to 100 micrometers, and these carbon materials are made into lithium support, To carbon material 88 weight section, polyvinylidene fluoride powder (binder) 12 weight section and N-methyl-pyrrolidone (organic solvent) 100 weight section were added and kneaded, and the homogeneous mixed paste was prepared. While applying this paste to 50-micrometer-thick copper foil uniformly, heating in temperature of 150 ** and removing an organic solvent, after drying, it pressed and the 50-micrometer-thick negative electrode material was produced.

[0026]The mixed solution of 1:1 of ethylene carbonate and diethyl carbonate was used as the electrolysis solution for this negative electrode material, vanadium oxide was used for the counter electrode, metal lithium was used for the reference pole, 3 pole cell was produced, and the charge and discharge test estimated the performance of the negative electrode material. The charge and discharge test was done by the constant current density of 50 mA/g, measured the service capacity of 1 cycle eye and a 100 cycle eye for charging stop potential and discharge stop potential as 0V and 1V, respectively, evaluated the performance as a negative electrode material, and showed the result in Table 2.

[0027]

[Table 2]

例No.		電池性能		
		放電容量Q(mAh/g)		サイクル特性
		1st (効率%)	100th (効率%)	Q_{100th}/Q_{1st} (%)
比	1	285 (73)	264 (99)	92.6
実	1	335 (84)	316 (99)	94.8
実	2	354 (83)	339 (99)	95.8
実	3	377 (85)	358 (99)	95.0
比	2	305 (78)	245 (99)	80.3
実	4	341 (83)	314 (98)	92.1
実	5	357 (85)	342 (99)	95.8
実	6	344 (86)	330 (99)	95.9
比	3	301 (78)	288 (99)	95.7
実	7	315 (83)	302 (99)	95.9
実	8	340 (82)	324 (98)	95.3
実	9	366 (86)	351 (99)	95.9

[0028]Carbon fiber of isotropy [carbon fiber / four to comparative example 6] Using [the Kureha Chemical Industry Co., Ltd. make and C-199T], others performed manufacture of a carbon material and production of a negative electrode material, and evaluation of battery capacity with the same technique as Examples 1-9, and showed those results in Table 3 and Table 4.

[0029]The actual carbon ratio of the comparative example 7 - 8 phenol resin was made into 40%, and also manufacture of a carbon material and production of a negative electrode material, and evaluation of battery capacity were performed with the same technique as Examples 1-9, and those results were shown in Table 3 and Table 4.

[0030]Changed into the comparative example 9 - 10 phenol resin, and the petroleum pitch was used, and also manufacture of a carbon material and production of a negative electrode material, and evaluation of battery capacity were performed with the same technique as Examples 1-9, and those results were shown in Table 3 and Table 4.

[0031]It is a pitch based carbon fiber, without laminating 11 to comparative example 12 thermosetting resin. The carbon material was manufactured using [the product made from Japanese Graphite fiber, and XN-40], and production of a negative electrode material and evaluation of battery capacity were performed with the same technique as Examples 1-9. The obtained result was shown in Table 3 and Table 4.

[0032]Phenol resin of 50% of 13 to comparative example 14 actual carbon ratio The result which the carbon material was manufactured using [the product made from Sumitomo DEYUREZU and PR940], and also was obtained by performing production of a negative electrode material and evaluation of battery capacity with the

same technique as Examples 1-9 was shown in Table 3 and Table 4.

[0033]

[Table 3]

例No.		炭素繊維種	被着樹脂種 *1	熱処理温度 (℃)	炭素材		
					重量比 *2	格子面間隔(nm)	
						炭素繊維部	樹脂炭化部
比	4	C-199T	Ph-1	2000	1.0/1	0.351	0.340
比	5	C-199T	Ph-1	2500	1.0/1	0.348	0.339
比	6	C-199T	Ph-1	3000	1.0/1	0.345	0.338
比	7	XN-40	Ph-2	2000	1.0/1	0.340	0.340
比	8	XN-40	Ph-2	2500	1.0/1	0.337	0.338
比	9	XN-40	ピッチ	2000	1.0/1	0.340	0.338
比	10	XN-40	ピッチ	2500	1.0/1	0.336	0.337
比	11	XN-40	——	2000	——	0.3402	——
比	12	XN-40	——	2500	——	0.3367	——
比	13	——	Ph-1	2000	——	——	0.3527
比	14	——	Ph-1	2500	——	——	0.3476

front notes *1 Ph-1; -- phenol resin Ph[of 50% of an actual carbon ratio]-2; -- phenol resin of 40% of an actual carbon ratio pitch; -- petroleum pitch resin Weight ratio of *2 resinous-coal ghost and carbon fiber[0034]

[Table 4]

例No.		電池性能		
		放電容量Q(mAh/g)		サイクル特性
		1st (効率%)	100th (効率%)	Q_{100th}/Q_{1st} (%)
比	4	235 (78)	221 (98)	94.0
比	5	264 (82)	244 (99)	92.4
比	6	279 (85)	263 (99)	94.3
比	7	259 (77)	238 (99)	91.9
比	8	286 (81)	263 (98)	92.0
比	9	245 (77)	231 (99)	94.3
比	10	272 (81)	257 (99)	94.5
比	11	230 (71)	196 (98)	85.2
比	12	265 (77)	220 (99)	93.0
比	13	201 (66)	191 (99)	95.0
比	14	234 (75)	220 (98)	94.0

[0035]As for the result of Table 1 - 4, service capacity exceeds 300 mAh/g and it also shows initial service capacity that each negative electrode material of an example which satisfies the requirements for this invention is large. Even if it repeats charge and discharge, there are few falls of service capacity, and it is accepted that the battery capacity excellent in cell capacity and a cycle characteristic is shown. On the other hand, the negative electrode material of a comparative example which separates from the requirements for this invention has small service capacity, and it turns out that initial service capacity is also in lower order.

[0036]

[Effect of the Invention]According to the negative electrode material of this invention, the surface of carbon fiber comprises 2-phase structure covered with the carbide of thermosetting resin as above, The value of lattice spacing (d_{002}) by a carbon fiber part d_{002}<0.343nm, When it has d_{002}<0.340nm graphite-crystals description in a resinous coal-ized part and a weight ratio with carbon fiber sets the coating volume of carbide as the range of 1:0.5-2, Even if service capacity is high and repeats charge and discharge, the negative electrode material for lithium secondary batteries with which the fall of service capacity has few outstanding battery capacities and cycle characteristics can be provided. According to the manufacturing method of this invention, it is possible to often manufacture the negative electrode material provided with the above-mentioned performance, and it is very useful as an industrial manufacturing method of the negative electrode material for lithium secondary batteries.